

KOKAI PATENT APPLICATION NO. SHO 63[1988]-17023

COMPOSITE FILM

[Translated from Japanese]

[Translation No. LP97829]

JAPANESE PATENT OFFICE (JP)

PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. SHO 63[1988]-17023

Technical Indication Section

Int. Cl. ⁴ :	B 29 C	47/06
		55/12
	B 32 B	27/36
	//B 29 K	67:00
	B 29 L	9:00

Identification code: 4F

Sequence Nos. for Office Use: 6660-4F
7446-4F
6762-4F

Application No.: Sho 61[1986]-162784

Application Date: July 10, 1986

Publication Date: January 25, 1988

No. of Inventions: 1 (Total of 6 pages)

Examination Request: Not requested

COMPOSITE FILM

[Fukugohkafuirumu]

Applicant: Diafoil Corp.
2-5-2 Marunouchi
Chiyoda-ku, Tokyo

Inventor: Shigeo Uchimi
c/o Diafoil Corp.
1000 banchi, Kamoshida-
machi, Mirori-ku
Yokohama-shi, Kanagawa-
ken

Agent: Hajime Hasegawa
Patent attorney
and 1 other

[There are no amendments to this patent.]

Specification

1. Title of the invention

A composite film

2. Claim of the invention

(1) A composite film produced by coextruding an inner layer consisting of an oriented film of copolymerized polyethylene-2,6-naphthalate that has a degree of orientation of the plane (ΔP) and a mean refractive index (\bar{n})¹ shown in relationship (1) below and which has surface layers consisting of oriented films essentially composed of polyethylene-2,6-naphthalate that have a degree of orientation of plane (ΔP) and a mean refractive index (\bar{n}) that satisfy the relationships shown in (2) and (3) where the thickness of the surface layer on each side is at least 5 μ .

¹Translator's note: \bar{n} is used in this translation in place of \bar{n}

$$\Delta P \leq 1.43 \cdot n - 2.136 \quad \dots (1)$$

$$n \geq 1.6660 \quad \dots (2)$$

$$\Delta P > 1.43 \cdot n - 2.136 \quad \dots (3)$$

3. Detailed explanation of the invention

[Field of industrial application]

The present invention pertains to a composite film. The present invention further pertains to a composite film produced by laminating an oriented film essentially composed of polyethylene-2,6-naphthalate on both surfaces of an oriented film composed of copolymerized polyethylene-2,6-naphthalate, which composite can be effectively used for applications in which heat resistance is required such as electrical insulation films, transparent conductive films, and floppy disks.

[Problems to be solved by the invention]

As all-purpose industrial films, oriented polyethylene terephthalate films are used for a wide variety of purposes, but increased heat resistance is required in many applications. For example, polyethylene terephthalate is ranked as a Class F film for electrical insulation applications, and a material capable of withstanding application temperatures is needed. Meanwhile, for transparent conductive films, film with a higher heat resistance and lower degree of deposition of oligomers than those of polyethylene terephthalate film and free from curling and oligomer deposition is needed. Furthermore, a film with higher heat resistance is in demand for floppy disks and for the development of higher deposition density perpendicular magnetization magnetic recording materials.

Many different types of heat resistance films have been suggested in an effort to meet the above-mentioned requirements, but polyethylene-2,6-naphthalate is the most promising candidate from the standpoint of cost and performance.

The inventor conducted considerable research on oriented polyethylene-2,6-naphthalate films, and as a result, discovered that oriented polyethylene-2,6-naphthalate films are far superior to oriented polyethylene terephthalate films in terms of heat resistance, oligomer content, and mechanical properties, etc. However, delamination is likely to occur in the above-mentioned film in the thickness direction possibly due to a high inplane orientation, and practical application has not been possible.

[Problems to be solved by the invention]

As a result of the continuous effort put forth by the inventor in an effort to produce a film capable of retaining excellent properties of oriented polyethylene-2,6-naphthalate films without the above-mentioned problems, for applications such as electrical insulation films, the present invention was accomplished.

In summary, the present invention is a composite film produced by coextruding an inner layer consisting of an oriented film of copolymerized polyethylene-2,6-naphthalate that has a degree of planar orientation (ΔP) and a mean refractive index (n) that satisfy the relationship shown in formula (1) and which has surface layers consisting of an oriented film essentially composed of polyethylene-2,6-naphthalate that satisfies the degree of planar orientation (ΔP) and mean refractive index (n) shown in formulas (2) and (3) wherein the

thickness of the surface layer on each side is at least 5 μ .

$$\Delta P \leq 1.43 \cdot n - 2.136 \quad \dots (1)$$

$$n \geq 1.6660 \quad \dots (2)$$

$$\Delta P > 1.43 \cdot n - 2.136 \quad \dots (3)$$

In the following, the present invention is explained in further detail.

In the present invention, the film made of a composed essentially of polyethylene-2,6-naphthalate means a polymer with a structural unit essentially composed of polyethylene-2,6-naphthalate, but as long as (3) and (2) below are satisfied, a small amount, for example, 3 mol% or less, of a third component may be copolymerized.

$$\Delta P > 1.43 \cdot n - 2.136 \quad \dots (3)$$

$$n \geq 1.6660 \quad \dots (2)$$

In this case, n is determined by equation (4), and in general, it is a value determined by the thermosetting temperature; thus, when the thermosetting temperature is high, n is higher.

$$n = 1/3 (n_{\alpha} + n_{\beta} + n_{\gamma}) \quad \dots (4)$$

(Wherein, n_{α} is the refractive index of the film in the thickness direction after biaxial

orientation and thermosetting, n_y is the maximum inplane refractive index of the same film, and n_p is the refractive index in the direction perpendicular to the y direction in the plane of the same film.)

When n is 1.620 or below, the coefficient of orientation and heat resistance are inadequate; thus, it is not desirable.

ΔP is the value determined by equation (5), and in general, it represents the degree of orientation in the inplane direction of the film. In other words, it indicates the degree of orientation of the naphthalene ring in the polyethylene-2,6-naphthalate parallel to the film plane.

$$n = 1/2 (n_\alpha + n_p) - n_y \quad \dots\dots (5)$$

(Wherein, definitions of n_α , n_p , and n_y are the same as in (4) above.)

In the case of a film in which ΔP and n do not satisfy (3), a high mechanical strength for the polyethylene-2,6-naphthalate cannot be achieved; thus, it is not suitable.

[p. 3]

On the other hand, the copolymerized polyethylene-2,6-naphthalate in the present invention means a polymer wherein 60 mol% to 99 mol% of the structure unit consists of ethylene-2,6-naphthalene and is copolymerized with 1 mol% to 40 mol%, preferably, 3 mol% to 40 mol%, of a third component. It is essential for the film made of the above-mentioned copolymerized polyethylene-2,6-naphthalate satisfies (1) below.

$$\Delta P \leq 1.43 \cdot n - 2.136 \quad \dots (1)$$

The objective of the present invention cannot be achieved when (1) is not satisfied even when a copolymerized film is used; thus, it is not suitable.

The polyethylene-2,6-naphthalate of the present invention can be produced by performing a condensation reaction for naphthalene-2,6-dicarboxylic acid or the ester thereof, for example, naphthalene-2,6-methyldicarboxylate, and ethylene glycol in the presence of an appropriate catalyst under appropriate reaction conditions. In this case, dicarboxylic acids such as adipic acid, oxalic acid, isophthalic acid, terephthalic acid, naphthalene-2,7-dicarboxylic acid, and diphenyl ether dicarboxylic acid, or lower alkylester thereof, oxycarboxylic acids such as p-oxybenzoic acid and p-oxyethoxybenzoic acid or lower alkylesters thereof, or dihydric alcohols such as propylene glycol, trimethylene glycol, tetramethylene glycol, and 1,4-cyclohexane dimethanol, polyalkylene glycols such as polyethylene glycol, polytetramethylene glycol, etc. can be used for the copolymer components.

Furthermore, blend polymers of the above-mentioned polyethylenes and other polymers can be used. For examples of polymers that can be used for blend polymers, many different types of polyethylenes that include polyamides, polyolefins, polycarbonates, can be mentioned. The amount of blend polymer used is 10 wt% or below for the above-mentioned polyethylene. Matting agents such as titanium dioxide, stabilizers such as phosphoric acid, phosphorous acid, and esters thereof, antioxidants such as hindered phenols, polymerization modifiers, crystallization modifiers, plasticizers, etc. may be

included during polymerization. Furthermore, organic lubricants such as sodium montanate, and hexamethylene bisstearylamine, and carbon blacks may be further included in the film.

When the degree of orientation of the polyethylene used in the present invention is too low, the mechanical strength becomes inadequate; thus, the ultimate viscosity of the material is at least 0.4, and preferably in the range of 0.55 to 0.9. In order to improve take-up ease and handling properties of the film during production of the film of the present invention, it is desirable to include a fine inert compound in the film layer composed essentially of polyethylene-2,6-naphthalate that structures the surface of the composite film to provide lubrication. As an example of a method that can be used in this case, a precipitation method wherein the residual metal compound that remains in the reaction system is reacted, for example, the residual metal compound that remains in the reaction system after the transesterification reaction, is reacted with phosphoric acid, etc. to precipitate fine particles. Also, the method referred to as the particle addition method wherein inert fine particles are mixed with polyethylene-2,6-naphthalate at a given stage during production of the polyethylene-2,6-naphthalate prior to extrusion in the film formation, can be used effectively. For example, at least one type of metal compound selected from among the group consisting of kaoline, talc, magnesium carbonate, barium carbonate, calcium sulfate, barium sulfate, lithium phosphate, calcium phosphate, magnesium phosphate, aluminum oxide, silicon oxide, titanium oxide, lithium fluoride, calcium oxalate, and terephthalates such as Ca, Ba, Zn, and Mn can be mentioned. As for removal of the large particles mixed among the particles added, or adjustment of the particle size, etc., these operations can be carried out by known methods, for example, the

air separation method, plain sedimentation separation in an ethylene glycol slurry or an aqueous slurry, centrifugal separation, pulverizing in a sand mill, etc. and/or a classification method, etc. can be used.

Also, the shape of the above-mentioned inert compound is not especially limited, and spherical, solid, and tabular forms can be used, and the hardness, specific weight, color, etc. are not especially limited.

[p. 4]

In general, the mean particle diameter of the above-mentioned inert compound is in the range of $0.1\ \mu$ to $10\ \mu$ in terms of the circle equivalent diameter, and in the range of $0.3\ \mu$ to $3\ \mu$ is especially suitable. The mixing ratio is in the range of 0.01 to 1 wt%, in the range of 0.02 to 0.8 wt% is preferable, and in the range of 0.03 to 0.5 wt% is especially desirable.

In this case, the mean surface roughness (Ra) of the above-mentioned composite film is not especially limited, and when used as a magnetic recording material, a range of 0.001 to $0.05\ \mu\text{m}$ is suitable, and a range of 0.003 to $0.03\ \mu\text{m}$ is preferable, and a range of 0.003 to $0.02\ \mu\text{m}$ is especially desirable. Furthermore, the ratio of large particles with a size that exceeds $1.16\ \mu\text{m}$ is $3.0/\text{cm}^2$ or less, preferably $2.0/\text{cm}^2$ or less.

The composite film of the present invention is a multilayer film essentially composed of polyethylene-2,6-naphthalate film and a copolymerized polyethylene-2,6-naphthalate film, and may be composed of three or more layers. However, it is essential for the surface layer to be a polyethylene-2,6-naphthalate layer. When the surface layer is not a polyethylene-2,6-naphthalate layer, the heat resistance of the film and the blocking of

precipitation of oligomers are inadequate.

Furthermore, in the composite film of the present invention, the thickness of each of the surface layers formed on either side is at least 5 μ , and a range of 5 μ to 150 μ is especially desirable. When [the thickness of] the surface layer essentially composed of polyethylene-2,6-naphthalate layer is 5 μ or below, adequate heat resistance of the copolymer layer cannot be achieved by the surface layer alone; on the other hand, when [the thickness] exceeds 150 μ , delamination of the surface layer essentially composed of polyethylene-2,6-naphthalate occurs; thus, in either case, it is not appropriate.

The primary objective of the present invention is to prevent delamination of the layer essentially composed of polyethylene-2,6-naphthalate layer, and the composite film of the present invention can be used effectively for production of a thick film. In other words, the composite film of the present invention can be effectively used for composite films having a total thickness for the layers of 30 μ or more, preferably, 50 μ or more, and even 70 μ or more.

Furthermore, in order to prevent curl, it is desirable to use the same composition and the same thickness for the layers essentially composed of polyethylene-2,6-naphthalate that form the surface layers in the three-layer structure.

In this case, the lamination method used to produce a structure of three or more layers, a method wherein the PEN film and copolymer PEN films are each produced separately and are bonded with an adhesive can be used, but when said method is used, it is difficult to maintain the surface flatness; thus, coextrusion using a die is preferred in this case. The laminated film produced by coextrusion is laminated in a non-stretched state;

thus, it is necessary to orient the film by stretching. For the orientation by stretching method used, a conventional process such as successive biaxial stretching wherein machine-direction stretching is performed by a roll followed by transverse stretching in a tenter, a biaxial stretching method wherein stretching is performed in both directions at the same time, and the repeat stretching method wherein a repeat stretch is performed in the machine direction or transverse direction after the above-mentioned biaxial stretching can be used. In this case, the stretching temperature used is preferably in the range of 110°C to 170°C, and the stretching ratio is preferably in the range of 2.0 to 6.0 times. It is desirable to perform heat setting for the above-mentioned biaxial stretched composite film at a temperature of 180°C or above but below the melting point, as needed.

The composite film produced above can be effectively used for electrical insulation and floppy disks as well as magnetic tapes, packaging, agricultural applications, photographic applications, adhesive tapes, building materials, decorative applications, etc. For example, packaging of food products, general cargo, and medical products, films used for greenhouses, single-coated or double-coated pressure-sensitive adhesive tapes, photographic films for printing, aerial photographic films, photographic films for copiers, 8-mm motion picture films, X-ray films, dry plate films, tracing films or copy films after matting process is performed, base films used for video or audio or 8 m/m video applications, base films for magnetic disks, base films for hot stamping, capacitors, transformers, coils, high-temperature magnet electric wires, flat wires, substrates for printed circuits, diaphragms for batteries such as fuel cells, seals, linings, protective clothing, films used for decorative boards, films used for walls, vibration films used for speakers, heat-

sensitive transfer films, membrane switches, substrates for solar batteries, substrates for liquid crystal panels, and furthermore, they can be laminate with other films, and used as composite materials with paper, metal, etc.

[p. 5]

[Application examples]

In the following, the present invention is further explained with application examples in specific terms, but the present invention is not especially limited to these application examples.

Evaluation methods used for the film are explained below.

(1) Refractive index

An Abbe refractometer (product of Atago Corp.) was used and the value of the Na-D line measured at 25°C was obtained.

Application Example 1

A polymer composed essentially of polyethylene-2,6-naphthalate with an ultimate viscosity of 0.65 and containing 0.18 wt% of spheroids with a mean particle diameter of 1.8 μ was used as raw material (A). Meanwhile, a polymer made of a copolymerized polyethylene-2,6-naphthalate with an ultimate viscosity of 0.63 and containing 3 mol% of terephthalic acid was used as a raw material (B). The above-mentioned raw material (A) and raw material (B) were dried separately, coextrusion was performed by a separate hot-melt extruders to form a three-layer structure with the raw material (B) as the inner layer and raw material (A) to form outer layers and casted onto a flat drum, cooled to solidify to

produce an amorphous sheet.

The above-mentioned sheet produced was then stretched to 4.0 times by a roll and heated by an infrared heater in the machine direction at 130°C; then, it was stretched to 4.0 times in the transverse direction at 135°C, and a heat set was further performed at 240°C. The film produced had a thickness of 250 μ , and was a three-layer film having an inner layer with a thickness of 190 μ , and each outer layer had a thickness of 30 μ . As for the refractive index of each layer, the value obtained for each of the raw materials stretched under the same conditions was used. Properties and evaluation results of the film produced are shown in Table I.

Application Examples 2 and 3

In the above-mentioned application example 1, the thickness of the inner layer was changed to 50 μ , and each outer layer to 10.0 μ and film formation was performed in the same manner (Application Example 2), and the thickness of inner layer was changed to 150 μ , and each outer layer to 50 μ , and film formation was performed in the same manner (Application Example 3). The results obtained are shown in Table I.

Comparative Example 1

Copolymer raw material (B) alone was used to form a film with a thickness of 250 μ and film formation was performed as in the case of Application Example 1. The results obtained are shown in Table I.

Comparative Example 2

Comparative Example 2

Polymer raw material (A) alone was used to form a film with a thickness of 250 μ and film formation was carried out as in Application Example 1. The results obtained are also shown in Table I.

[p. 6]

Table I

	Film properties						Total thickness (μ)	Properties of product (*)	
	Outer layer			Outer layer				Delamination properties	Buckling properties
	Thickness (μ)	n	Δ P	Thickness (μ)	n	Δ P			
Application Example 1	190 μ	1.6680	0.245	30 μ	1.6700	0.262	250 μ	●	○
Application Example 2	50 μ	1.6680	0.245	100 μ	1.6700	0.262	250 μ	○	●
Application Example 3	150 μ	1.6680	0.245	50 μ	1.6700	0.262	250 μ	●	●
Comparative Example 1	250 μ	1.6680	0.245	—	—	—	250 μ	●	x
Comparative Example 2	250 μ	1.6700	0.262	—	—	—	250 μ	x	●

(*) Delamination and buckling properties of the film produced were examined as the film was inserted as a slot or wedge of a motor.

[Effect of the invention]

The composite film of the present invention is free from delamination, and the film can be effectively used for thick film applications.

Applicant: Diafoil Corp.

Agent: Hajime Hasegawa, Patent attorney

and 1 other